Conference report

Gold Highlights at the 21st Meeting of the Portuguese Society of Chemistry in Porto, Portugal, June 11-13, 2008

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There were over 300 participants attending this meeting, mostly native Portuguese and foreigners doing research in Portugal, coming from several chemistry areas. However some visitors were also present from Spain, France, United Kingdom, Slovenia, Brazil, Argentina, USA and India. The majority of participants were from Universities and Research Institutes; but some representatives from industry and secondary schools were also present. This year's conference was concerned with 'Chemistry and Innovation' and dealt with the innovation in chemical industry to develop new products, technologies and processes, innovation in the teaching of chemistry and chemical engineering and innovation at the interface between chemistry and other subjects.

Gold-related subjects were represented by 1 oral presentation and 8 posters, which was just a 'drop in the ocean' when compared with about 50 orals and 240 poster presentations in total, but revealed that this Southern European country is already doing some research on this very important subject. This is particularly significant, when compared with the previous biannual meetings in 2006 (where only 4 gold posters were presented and 3 of them came from the same groups present in this year's meeting) and 2004 (where only one poster dealt specifically with gold). Potential applications for the advances in the technology described in this year's conference are indicated here.

Inês Gomes (New University of Lisbon) presented a poster entitled 'Characterization of bionanoprobes from cytochrome *c*/ gold nanoparticle complexes'. In this work, gold nanoparticles (AuNPs) were coated with two citochromes *c* isolated from horse heart (HCc) and yeast (YCc). In the complexes, HCc is most probably electrostatically bound to the gold surface through its lysine patch, whereas YCc is probably covalently bound to the gold surface by the sulfur atom of its cysteine-102 residue. It was shown that both cytochrome *c*-AuNP complexes aggregate when the pH of the solution is low, inducing a colour change from red (non-aggregated complexes, at high pH) to blue (aggregated complexes, at low pH). This behaviour was specific to cytochrome *c* alone. Significant conformational changes in the proteins secondary structure in the YCc-AuNP complex were seen, whereas HCc-AuNO complex exhibited no noteworthy alterations. The protein layer of the HCc-AuNP complex was ~2 nm, and ~4 nm for the YCc complex. For the latter, the protein layer proved to be easily removed by sample drying, in contrast with the more sturdy protein layer of the former. In both cases, the surface potential was similar. Thus, the binding mode of the two proteins to the AuNPs was different and that conferred distinctive properties to the AuNP-cytochrome *c* complexes. This modulation of the surface properties of these AuNP-protein complexes is potentially useful from the point of view of the fabrication of bionanoprobes.

Ricardo Franco, from the same group, gave an oral presentation dealing with 'pH-induced adsorption of cytochrome *c* to acidic self-assembled monolayers on gold surfaces and nanoparticles'. The adsorption characteristics HCc onto self-assembled monolayers of mercaptoundecanoic acid (MUA) on gold surfaces and AuNPs were studied. At pH 7.4 and 4.5 the presence of MUA favours protein adsorption at the higher pH but does not significantly influence the process at lower pH values. AuNP/MUA/HCc bionanoprobes and AuNP/MUA complexes show aggregation as a function of the solution pH, inducing a shift of the AuNP plasmon band corresponding to a red-to-blue colour change in the solution. This behaviour was not observed in the AuNPs and protein alone. AuNP/MUA/HCc bionanoprobes aggregate at pH 6.5, whereas AuNP/MUA aggregate at pH 4.5. Therefore, HCc adsorbs onto MUA self-assembled monolayers on Au surfaces and nanoparticles in an electrostatic and pH-dependent manner. Furthermore, the amount of HCc on the Au surface can be modulated by the pH value of the solution, with 7.4 being the 'switching pH' value.

Sónia Carabineiro (Faculty of Engineering, University of Porto) presented a poster on 'Gold nanoparticles on ceria supports for the oxidation of carbon monoxide'. Ultrafine platelet shaped CeO_2 particles were prepared by the solvothermal method (150°C, autogeneous pressure, 150 min) using methanol and CTAB. Au was loaded onto the ceria supports by Incipient Wetness (IW) impregnation, Double Impregnation (DIM) and Liquid Phase Reductive Deposition (LPRD)[2]. A commercial CeO_2 (Fluka) was also used for comparison. The DIM method produced very small gold particles (1-2 nm) and gave the best results. Samples prepared by LPRD and IW gave larger sizes (up to ~10 and ~20 nm, respectively), which can explain their lower activity in CO oxidation.

Junjiang Zhu, from the same group, presented a poster on 'Carbon supported catalysts for alcohol oxidation with

molecular oxygen'. In this work Co/C catalysts prepared by incipient wetness impregnation were compared with Au/C catalysts prepared by the Au sol method described in the literature[3]. Catalytic tests using benzyl alcohol followed a reported protocol for Au/C catalysts, using basic conditions[4], while for Co/C catalysts no strong base was added. Both the activity and the selectivity did not change much from re-use of Au/AC catalyst even after four cycles (conversion = 86.8%, selectivity = 88.5%). The Co/C catalysts were found to be less active than Au/C, but the former did not need the aid of a strong base.

Carla Arieira (Faculty of Sciences, University of Porto) presented a poster on 'Assemblies of gold nanoparticles prepared by using sugars as reducing agents'. The aim of this work was the study of electrodes modified by deposition of gold nanoparticles for electrochemical sensing. Nanoparticles of gold were prepared using a number of reducing sugars, such as glucose, sucrose, sorbitol, manitol and dulcitol, and stabilized with various ligands such as citrate, lysine and cytosine. The UV spectra of the Au solution obtained displayed a maximum of 523 nm indicative of the presence of nanoparticles. When glucose, sorbitol, manitol and dulcitol were used as reducing agents, λ maximum did not change, suggesting that the size distribution of the nanoparticles formed was similar for all these sugars. In contrast, when sucrose was used, the intensity of the maximum indicated a higher concentration of nanoparticles, suggesting that this sugar is the most efficient reducing agent. AuNPs were deposited on a GC electrode surface and the voltametric profile was obtained, showing that the redox process becomes irreversible in the presence of the AuNPs. This is probably caused by surface electrostatic repulsions between AuNPs and the negatively charged probe. Work is still in progress to confirm this interpretation.

Elisa Pereira, from the same University, presented a poster on 'AFM characterization of the organized molecular films'. In this work, Langmuir–Blodgett (LB) films were prepared by spreading a chloroform solution of Au NPs on a sub-phase kept at 20°C. The monolayer was compressed at the speed of 10 mm/min. After compression of monolayer to 15 mN/m, this was transferred onto a mica substrate by dipping the substrate onto a monolayer at a deposition rate of 5 mm/min.

The gold oleyl amine (OLA) functionalized nanoparticles were prepared as described in the literature[5]. Application of the self-assembled monolayer (SAM) technique consists in the immobilization of the gold nanoparticles modified with OLA and subsequent deposition of the DNA molecules on mica. The steps of the deposition were analysed by AFM, resulting in a transition from three-dimensional to a two-dimensional conformation, limited by the thickness of the layer.

Maria Adelaide Miranda, from the same University, had a poster presentation on 'Anisotropic gold nanoparticles: a controlled approach to obtain nanotriangles'. By the photocatalytic reduction of hydrogen tetrachloroaurate(III) by triethanolamine using Sn(IV) meso-tetra(N-Methyl-4pyridyl)porphine tetratosylate chloride as the photocatalyst, and CTAB as the capping agent, in an aqueous medium (pH=6.5-8.0), beautiful gold nanotriangles were obtained. It was shown that the pH and the concentration of CTAB and SntMepyP have a strong influence on the morphology of the nanoparticles. These factors were optimized for the preparation of nanotriangles with a length of ~147 nm and 15-19 nm height.

Pedro Quaresma (New University of Lisbon) presented a poster in collaboration with the University of Porto, entitled 'Gold on magnetite nanoparticles: growth to a core-shell system'. In this work, magnetite nanoparticles of Fe_3O_4 were produced using an acetylacetonate metal precursor, resulting in enhanced control over size and monodispersity. An ultrasound mediated iterative addition of gold precursor and reducing agent was employed for the in situ formation of gold nuclei on the surface of magnetite nanoparticles and its growth to a gold shell layer.

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References

1 M. Bowker, A. Nuhu and J. Soares, *Catal. Today*, 2007, **122**, 245
2 Y. Sunagawa, K. Yamamoto, H. Takahashi and A. Muramatsu, *Catal. Today*, 2008 , **132**, 81
3 Y. Onal, S. Schimpf and P. Claus, *J. Catal*., 2004, **223**, 122
4 J.J. Zhu, J.L. Figueiredo and J.L. Faria, *Catal. Commun*., 2008, **9**, 2395
5 M. Aslam, L. Fu, M. Su, K. Vijayamohanan and V.P. Dravid, *J. Mater. Chem*., 2004, **14**, 1795